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CONDITIONS FOR FORMATION OF CONDUCTING ALUMINUM-BEARING COATINGS

V. V. Tavgen',[1] E. V. Shinkareva,[1] and Yu. G. Zonov[1]

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The conditions for the formation of conducting coatings based on a composite containing aluminum powder and barium-aluminum borate glass are investigated. It is demonstrated that additional introduction of chromium oxide makes it possible after heat treatment at 660 – 750°C to obtain coatings with a surface resistivity of 0.05 – 0.50 Ω · cm on various enameled substrates.

Film heating elements (FHE) attract the attention of researchers in the context of the possibility of developing more sophisticated electrical heaters, both household and industrial. Structurally, a FHE constitutes a steel substrate coated with dielectric glass enamel, on the surface of which a resistive film is deposited, according to a specific pattern. The combination of heat-generating and heat-liberating surfaces in the same element ensures significant design advantages. However, this design calls for a glass enamel and a resistive film which would satisfy stringent requirements. The glass enamel or glass ceramic coating ought to have low thickness (100 – 300 μm) and at the same time ensure high dielectric parameters (resistance and electric strength) up to the service temperatures of the electric heater. The chemical composition of dielectric coatings is designed accordingly. They are, as a rule, alkali-free glass ceramic coatings. However, in some cases involving weakly loaded low-voltage and low-temperature FHE, it is convenient to use industrially produced glass enamel coatings, for example, white enamel ÉSP-117 (GOST 24405–80).

The resistive (conducting) film is a composite coating, which consists of metal powders and an inorganic binder represented by low-melting glass, phosphate, or silicate. Heat treatment generates a structure providing for the required resistance of the coating and its reliable adhesion to the dielectric substrate. In producing low-ohm conducting films with the resistivity 0.05 – 0.50 Ω · cm, it is possible to replace expensive chromium, titanium, and nickel powders by a composition of aluminum powder and liquid sodium glass [1]. It is advisable to deposit aluminum-bearing films by silk screen printing or decalcomania, which makes it possible to mechanize the process and improves the reproducibility of the resistivity value. In testing this technology, it was found that the resistance of glass-aluminum film produced by heat treatment at 600 – 700°C depends not only on the initial ingredient composition, but also on the chemical composition of the vitreous substrate.

The purpose of the present study was to determine the optimum conditions for the production of conducting aluminum-bearing coatings on steel enameled substrates.

The initial materials for conducting coatings were aluminum powder PA-VCh (TU 48-5-172–77) with the particle size below 50 μm, alkaline barium-aluminoborate glass (with the softening point 505°C), and organic binders used in silk screen printing. The transfer designs (decals) of the conducting coatings were obtained using the decalcomania method. The decals were applied to the dielectric substrate made of glass enamel ÉSP-117. The conducting coating thickness was 100 μm. The resistivity of the coatings was measured with an Shch-4300 combined device. The x-ray patterns of the conducting coating surface were recorded on a DRON-3 diffractometer (CuK_α radiation, Ni filter). The differential thermal analysis of the powder composition was carried out in a corundum crucible, employing a MOM derivatograph with a rate of temperature rise of 10 K/min and a sample weight of 800 mg. The reference standard was calcined aluminum oxide of "chemically pure" grade.

It was found that the resistivity of the composite aluminum-bearing coating to a large extent depends on the chemical composition of the substrate, in particular, on the content of chromium oxide in the substrate. Thus, the composite coating consisting of 80% (here and elsewhere weight content indicated) PA-VCh powder and 20% glass binder deposited on white titanium enamel ÉSP-117 and heat-treated in the temperature interval 660 – 800°C has a specific surface resistance equal to 1.6×10^5 Ω · cm. The same composite

[1] Institute of General and Inorganic Chemistry, National Academy of Sciences, Minsk, Belarus.

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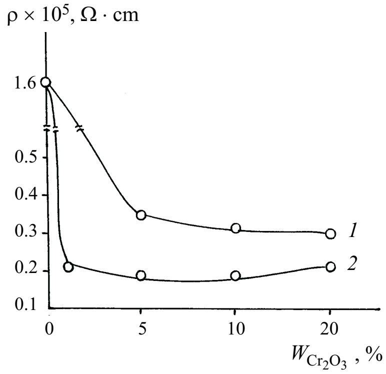

Fig. 1. Specific surface resistance of coating versus the chromium oxide content in the substrate, namely, glass enamel ÉSP-117 (*1*) and in the conducting coating (*2*) formed on ÉSP-117 enamel at 660°C for 10 min.

coating applied to glass enamel 12p (USSR Inventors' Certif. No. 1447762), which contains around 1% chromium oxide, has a specific resistance of 0.5 $\Omega \cdot$ cm. It was found that an introduction of chromium oxide into the white enamel ÉSP-117 or into the composite aluminum-bearing coating produces a significant decrease in the resistivity of the latter (Fig. 1).

The DTA curve of aluminum powder (Fig. 2) exhibits an endothermic effect in the temperature range 530 – 700°C with a minimum at 660°C determined by the melting of aluminum. As the temperature rises above 700°C, the sample weight slightly grows, which points to the oxidation of aluminum and the formation of a small quantity of α-Al_2O_3. It should be noted that heat treatment of pure aluminum powder at 700 – 800°C, i.e., above the aluminum melting point, does not lead to the merging of drops and the emergence of continuous spread. Only surface oxidation and sintering of grains via the oxide layer take place, whereas the emerging cake after cooling becomes brittle and gets destroyed rather easily.

Adding barium-aluminoborate glass to the powder initiates the oxidation of aluminum at low temperatures (585, 705°C), which is presumably due to the dissolution of the oxide film in the glass melt. An introduction of chromium oxide in the glass-aluminum composite further activates the oxidation of aluminum, especially at temperatures above 700°C. It can be assumed that Cr_2O_3, which is a surfactant oxide, in glass melts [2] accelerates the dissolution of Al_2O_3 oxide film from the surface of aluminum grains, thus facilitating the formation of continuous conducting aluminum-bearing structures. This assumption agrees with the fact that the coating containing 76% aluminum, 19% barium-aluminoborate glass, and 5% Cr_2O_3 and fired at temperatures below 600°C has high resistivity: 10^{10} $\Omega \cdot$ cm, whereas the coating fired at 660 – 750°C has a resistivity of 0.05 – 0.08 $\Omega \cdot$ cm.

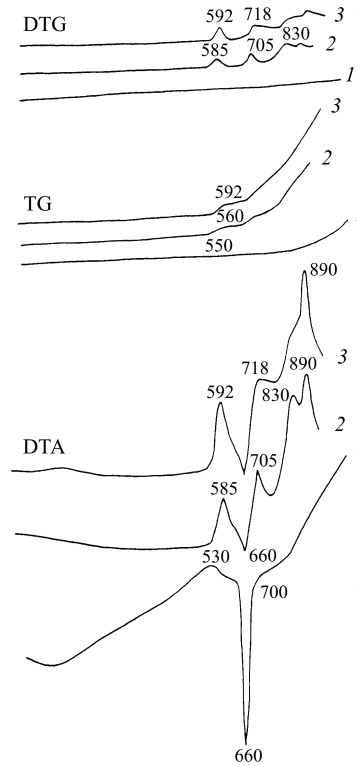

Fig. 2. Derivatograms of aluminum powder sample (*1*) and samples of composites containing 20% glass + 80% Al (*2*) and 20% glass + 75% Al + 5% Cr_2O_3 (*3*).

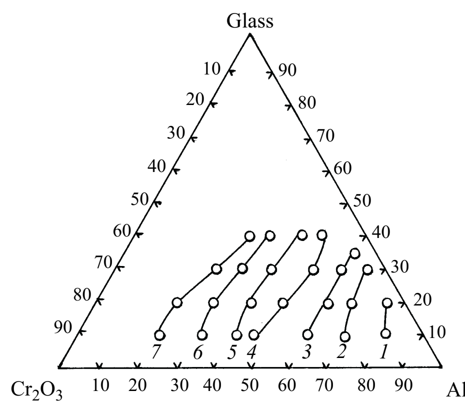

Fig. 3. Specific surface resistance of coatings of the system Cr_2O_3 – barium-aluminoborate glass – Al heat-treated at 660°C for 10 min (the substrate is glass enamel ÉSP-117 containing 5% Cr_2O_3). Specific surface resistance of coatings: *1*, *2*, *3*, *4*, *5*, *6*, and *7*) 0.05, 0.08, 0.20, 0.50, 5.00, 73.00, and 1.4×10^6 $\Omega \cdot$ cm, respectively.

The study of the electrophysical properties of composite coatings of the chromium oxide – barium-aluminoborate glass – aluminum system revealed that there exists an extensive range of compositions, in which conducting coatings with low resistivity are formed (Fig. 3), both on glass enamel ÉSP-117 and on other substrates. The composite coatings based on the composition containing 35 – 80% aluminum

powder, 10 – 40% barium-aluminoborate glass, and 5 – 50% chromium oxide after firing at 660 – 750°C acquire sufficient adhesion to the glass enamel substrate, have low resistivity (0.05 – 0.50 Ω · cm), and preserve stable parameters in long-time service up to 300°C.

Thus, the aluminum – barium-aluminoborate glass – chromium oxide composite system can be used to produce conducting coatings with low surface resistivity (0.05 – 0.50 Ω · cm). The coatings are applied to enameled steel substrate by the decalcomania method, and after firing at 660 – 750°C they acquire sufficient adhesion to the substrate, whereas the chromium oxide additive facilitates the formation of continuous aluminum-bearing structures.

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